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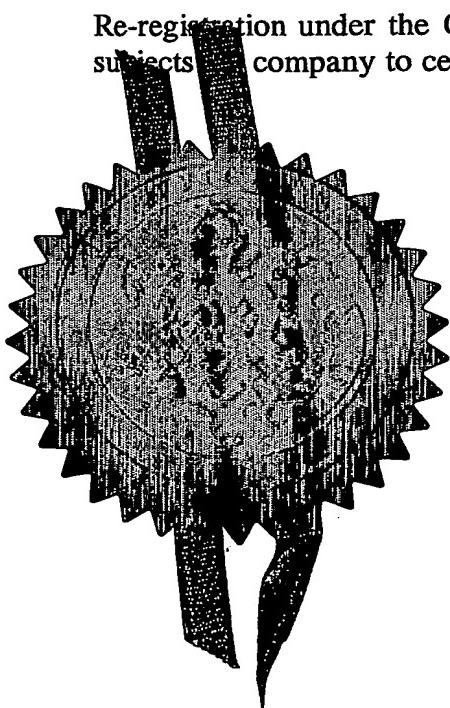
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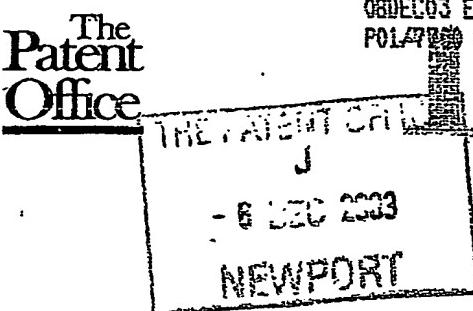
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Dated 27 October 2004

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Patents ADP number <i>(if you know it)</i>			
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SMC 60634

APPLICANTS

AVECIA LIMITED

TITLE

PROCESS

PROCESS

This invention relates to a process for preparing an encapsulated particulate solid and to the use of such solids in inks, especially inks for use in ink jet printing.

Many inks, mill-bases, paints and the like require effective dispersants for uniformly distributing a particulate solid in a liquid vehicle. The liquid vehicle may vary from highly polar (e.g. water) to highly non-polar liquids (e.g. toluene). Known dispersants tend to work effectively only with liquid vehicles within a range of polarities. Outside such polarities the particulate solid typically flocculates. Thus a range of dispersants has been developed for liquid media of different polarities.

Conventional dispersants suffer from a disadvantage in that they may readily be displaced from a particulate solid surface by a more strongly absorbing material which can result in destabilisation of the dispersion and flocculation.

The problems associated with conventional dispersants can be addressed in part by encapsulating a particulate solid within a cross-linked dispersant. The process of encapsulating a particulate solid with a cross-linked dispersant is typically performed in a liquid medium. A cross-linkable dispersant can be mixed with a particulate solid distributed in a liquid medium, the dispersant then absorbs onto the particulate solid surface and the dispersant can then be cross-linked via its cross-linkable groups utilising a cross-linking agent to "fix" the dispersant onto the particulate solid surface. Such an approach is described in US 6262152, WO 0020520, JP 199710483, JP 1999152424 and EP 732381. We have found such encapsulation approaches suffer from deficiencies. For example in US 6262152 and WO 0020520 the cross-linking chemistry described involves the reaction between isocyanate groups in the cross-linking agent and hydroxy groups in the dispersant. Hydrophobic cross-linking agents are disclosed in US 6262152 and WO 0020520 but such cross-linking agents tend to be difficult to disperse into liquid media and result in a significant degree of flocculation and an increase in the particle size of the particulate solid. JP 199710483 describes an acid precipitation and redispersion process which typically utilises melamine cross-linking. JP 199710483 also describes harsh curing conditions of around 95°C combined with an acid catalyst needed to get the cross-linking chemistries to cure. In JP 1999152424 a similar process of acid precipitation and redispersion is described. Here even harsher cure temperatures of around 140°C are typically used to effect cure. These harsh conditions tend to flocculate the pigment dispersion.

EP 732381 describes isocyanate cross-linking agents, amine cross-linking agents and hydroxy prepolymer dispersants as a reactive cross-linking system. The reaction typically requires a temperature of around 80°C. A solvent is needed in the dispersion process to dissolve the dispersant. The solvent is then typically removed from the final product. These thermal conditions and the presence of a solvent tend, again, to result in flocculation of the particulate solid.

According to the present invention there is provided a process for preparing an encapsulated particulate solid comprising cross-linking a dispersant with a cross-linking agent in the presence of a particulate solid and a liquid medium, thereby encapsulating the particulate solid within the cross-linked dispersant, characterised in that:

- 5      a) the dispersant has at least one cross-linkable group selected from keto, aldehyde and beta-diketoester groups; and
- b) the cross-linking agent has at least two cross-linking groups reactive towards said cross-linkable group(s).

## 10      PARTICULATE SOLID

The particulate solid may be any inorganic or organic particulate solid material or mixture thereof which is insoluble in the liquid medium. Preferably the particulate solid is a colorant, more preferably a pigment.

Examples of suitable particulate solids are inorganic and organic pigments, extenders, fillers for paints and plastics materials; disperse dyes and water-soluble dyes in liquid media which do not dissolve said dyes; optical brightening agents; textile auxiliaries for solvent dyebaths, inks and other solvent application system; solids for oil-based and inverse-emulsion drilling muds; particulate ceramic materials; and magnetic particles (e.g. for use in magnetic recording media) biocides; agrochemicals; and pharmaceuticals.

A preferred particulate solid is an organic pigment, for example any of the classes of pigments described in the Third Edition of the Colour Index (1971) and subsequent revisions of, and supplements thereto, under the chapter headed "Pigments". Examples of organic pigments are those from the azo (including disazo and condensed azo), thioindigo, indanthrone, isoindanthrone, anthanthrone, anthraquinone, isodibenzanthrone, triphendioxazine, quinacridone and phthalocyanine series, especially copper phthalocyanine and its nuclear halogenated derivatives, and also lakes of acid, basic and mordant dyes. Carbon black, although often regarded as being inorganic, behaves more like an organic pigment in its dispersing properties and is another example of a suitable particulate solid. Preferred organic pigments are phthalocyanines, especially copper phthalocyanine pigments, azo pigments, indanthrones, anthranthrones, quinacridones and carbon black pigments.

Preferred inorganic particulate solids include: extenders and fillers, e.g. talc, kaolin, silica, barytes and chalk; particulate ceramic materials, e.g. alumina, silica, zirconia, titania, silicon nitride, boron nitride, silicon carbide, boron carbide, mixed silicon-aluminium nitrides and metal titanates; particulate magnetic materials e.g. magnetic oxides of transition metals, especially iron and chromium, e.g. gamma- $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ , and cobalt-doped iron oxides, calcium oxide, ferrites, especially barium ferrites; and metal particles, especially metallic iron, nickel, cobalt and alloys thereof.

Where the process of the present invention is used to make encapsulated particulate solids for use in ink jet inks the pigment is preferably a cyan, magenta, yellow or black pigment.

5 LIQUID MEDIUM

The liquid medium may be non-polar but is preferably polar. "Polar" liquids are generally capable of forming moderate to strong bonds, e.g. as described in the article entitled "A Three Dimensional Approach to Solubility" by Crowley et al in Journal of Paint Technology, Vol. 38, 1966, at page 269. Polar liquid media generally have a hydrogen bonding number of 5 or more as defined in the abovementioned article.

10 Examples of suitable polar liquid media include ethers, glycols, alcohols, amides and especially water. Numerous specific examples of polar liquid media are given in the book entitled "Compatibility and Solubility" by Ibert Mellan (published in 1968 by Noyes Development Corporation) in Table 2.14 on pages 39-40, which is incorporated herein by reference thereto.

15 Preferred polar liquid media are alkanols, especially such liquids containing up to, and including, a total of 6 carbon atoms. As examples of the preferred polar liquid media there may be mentioned glycols and glycol esters and ethers, e.g. ethylene glycol, 2-ethoxyethanol, 3-methoxypropylpropanol, 3-ethoxypropylpropanol; alkanols, e.g. methanol, ethanol, n-propanol, isopropanol, n-butanol and isobutanol; cyclic ethers and amides, especially cyclic amides, e.g. pyrrolidone and n-methyl pyrrolidone; more especially water; and combinations thereof.

20 The polar liquid medium is optionally a polyol, that is to say, a liquid with two or more hydroxy groups. Preferred polyols include glycerol, alpha-omega diols and especially alpha-omega diol ethoxylates.

25 Preferably the liquid medium comprises water as this tends to result in a particularly stable and fine encapsulated particulate solid. Preferably the liquid medium comprises from 1 to 100%, more preferably from 10 to 100%, especially from 20 to 90% and more especially from 30 to 80% water by weight.

30 Preferred non-polar liquid media include non-halogenated aromatic hydrocarbons (e.g. toluene and xylene); halogenated aromatic hydrocarbons (e.g. chlorobenzene, dichlorobenzene and chlorotoluene); non-halogenated aliphatic hydrocarbons (e.g. linear and branched aliphatic hydrocarbons containing six or more carbon atoms, including fully and partially saturated), halogenated aliphatic hydrocarbons (e.g. dichloromethane, carbon tetrachloride, chloroform, trichloroethane); natural non-polar liquids (e.g. vegetable oil, sunflower oil, linseed oil, terpenes and glycerides); and combinations thereof.

35 The liquid medium may comprise a mixture of liquids which may be polar or non-polar liquids. It is preferred that at least one component of the liquid medium is a polar liquid.

Preferably the liquid medium is not reactive towards either the cross-linking agent or the dispersant. Thus it is preferred that the liquid medium is free from components having amine, imine, thiol, (meth) acrylate, activated olefin, hydrazide, keto, aldehyde or beta-diketoester groups. In the case of amine groups tertiary or stearically hindered amine groups may be present in the liquid medium as these are essentially non-reactive groups

5

#### DISPERSANT

Preferably the dispersants is polymeric, e.g. a polyurethane, polyester or more preferably a polyvinyl dispersant or a combination thereof. The dispersant must have at 10 least one, more preferably at least two cross-linkable keto, aldehyde and/or beta-diketoester groups.

The above mentioned cross-linkable groups are preferably incorporated into the dispersant by means of copolymerising a monomer containing at least one keto, aldehyde or beta-diketoester group. For polyvinyl dispersants the preferred monomers containing at 15 least one keto, aldehyde or beta-diketoester group are acrolein, methyl vinyl ketone, diacetone acrylamide and especially acetoacetoxy ethylmethacrylate. Hence preferred polyvinyl dispersants comprise at least one residue of such monomers.

Polyesters containing at least one beta-diketoester groups can be prepared by reacting a polyester having one or more primary hydroxy groups with a suitable chloro, 20 bromo or iodo-alky acetoacetate or dieketene. Polyurethanes containing at least one beta-diketoester groups can be prepared in an analogous way to the above polyesters using one or more primary hydroxy groups in the polyurethane. Such functionalisation routes are well known in the literature, for example J.Coating Technology 62, (789), 101, (1990). Alternatively keto and aldehyde groups may readily be prepared by the reduction 25 of a carboxylic acid or by the oxidation of an alcohol.

Preferably the monomer containing at least one keto, aldehyde or beta-diketoester group is incorporated at from 80 to 0.1 mole%, more preferably from 70 to 5 mole% and especially from 70 to 10 mole% based on all the monomers used to make the dispersant.

30 Preferred polymeric dispersants comprise both hydrophilic and hydrophobic monomers.

The polymeric dispersants are preferably random (having statistically short blocks or segments) but can be alternating, block, graft or star (having longer blocks or segments). The polymeric dispersants can be branched or star but are preferably linear. 35 The polymeric dispersants may have two or more segments but are preferably random.

In embodiments where the dispersant has two or more segments it is preferred that at least one segment is hydrophobic and at least one segment is hydrophilic relative to each other. A preferred method for making hydrophilic and hydrophobic segments is by the polymerisation of hydrophilic and hydrophobic monomers respectively. Where the 40 dispersant has at least one hydrophilic and at least one hydrophobic segment the cross-

linkable group can be situated in a hydrophobic segment, in a hydrophilic segment or in both.

Hydrophilic monomers are those monomers comprising hydrophilic groups which may be ionic or non-ionic groups. The ionic groups may be cationic but are preferably anionic. Both cationic and anionic groups may be used to give amphoteric stabilisation. Preferred anionic groups are phenoxy, carboxylic acid, sulphonic acid and phosphoric acid groups which may be in the free acid or salt form. Preferred salts forms are ammonium, substituted ammonium, quaternary ammonium, sodium, lithium and potassium salts.

Preferred cationic groups are substituted ammonium, quaternary ammonium, benzalkonium, guanidine, biguanidine and pyridinium. These can be in the form of a free base, a salt such as a hydroxide, sulphate, nitrate, chloride, bromide, iodide and fluoride or in the form of a quaternary ammonium salt formed with for example an alkyl halide or dimethyl sulphate.

Preferred non-ionic groups are glucosides, saccharides, pyrrolidone, acrylamide residues and especially alkyleneoxy (e.g. propyleneoxy, ethyleneoxy and combinations thereof) and hydroxy groups. The dispersant can contain a single non-ionic group, several non-ionic groups throughout the dispersant or one or more polymeric chains containing non-ionic groups. Hydroxy groups can be incorporated using polymeric chains such as polyvinylalcohol, polyhydroxyl functional acrylics and celluloses. Alkyleneoxy groups can be incorporated using polymeric chains such as polyethyleneoxide, polypropyleneoxide and polyethyleneoxide-co-polypropyleneoxide.

Hydrophobic monomers are those monomers comprising hydrophobic groups. Preferred hydrophobic groups are predominantly hydrocarbons, fluorocarbons and alkyl siloxanes comprising less than three and more preferably no hydrophilic groups. The hydrophobic group is preferably a C<sub>3</sub>-C<sub>50</sub> chain which can be pendant or in chain with the hydrophobic monomer.

Polyvinyl dispersants may be made by any means known in the art. A preferred method for making polyvinyl dispersants is free radical polymerisation of vinyl monomers, especially (meth)acrylates and vinyl monomer containing aromatic groups such as vinyl naphthalene and especially styrenic monomers. Suitable free radical polymerisation methods include but are not limited to suspension, solution, dispersion and preferably emulsion polymerisation.

Vinyl copolymers which contain the residue of both hydrophilic and hydrophobic monomers can be made essentially without segments. Using cost effective, conventional and robust free radical polymerisation methods the segment length is often statistically very short or effectively non existent. This is the case in what are often referred to as "random" polymerisations. Thus in order to produce less preferred segment structures with longer segment lengths more exotic and more costly polymerisation methods such as living polymerisations and especially group transfer polymerisation, atom transfer

polymerisation, macromonomer polymerisation, graft polymerisation and anionic or cationic polymerisation are required

Suitable hydrophilic vinyl monomers include non-ionic and ionic monomers.

Preferred non-ionic vinyl monomers are those containing saccharide, glucoside, amide, pyrrolidone and especially hydroxy and ethoxy groups.

Preferred examples of non-ionic vinyl monomers include hydroxy ethylacrylate, hydroxy ethyl methacrylate, vinyl pyrrolidone, ethoxylated (meth)acrylates, (meth)acrylamides and etheneoxy-propyleneoxy functional (meth)acrylates.

The ionic vinyl monomer may be cationic but is preferably anionic. Preferred anionic vinyl monomers are those comprising phosphoric acid groups, sulphonic acid groups and especially carboxylic acid groups which may be in the free acid (protonated) form or salts thereof. The salts are as described hereinbefore. Preferred examples are acrylic acid, methacrylic acid, itaconic acid,  $\beta$ -carboxy ethyl acrylate, maleic acid, monoalkyl itaconates (for example, monomethyl maleate, monoethyl maleate, monobutyl maleate and monoctyl maleate), citraconic acid, styrenesulfonic acid, vinylbenzylsulfonic acid, vinylsulfonic acid, acryloyloxyalkyl sulfonic acids (for example, acryloyloxyethyl sulfonic acid, acryloyloxyethyl sulfonic acid, acryloyloxypropyl sulfonic acid and acryloyloxybutyl sulfonic acid), methacryloyloxyethyl sulfonic acid, methacryloyloxyethyl sulfonic acid, methacryloyloxypropyl sulfonic acid and methacryloyloxybutyl sulfonic acid), 2-acrylamido-2-alkylalkane sulfonic acids (for example, 2-acrylamido-2-methylethanesulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid and 2-acrylamido-2-methylbutane sulfonic acid), 2-methacrylamido-2-alkylalkane sulfonic acids (for example, 2-methacrylamido-2-methylethanesulfonic acid, 2-methacrylamido-2-methylpropanesulfonic acid and 2-methacrylamido-2-methylbutanesulfonic acid), mono-(acryloyloxyalkyl)phosphates (for example, mono(acryloyloxyethyl)phosphate and mono(3-acryloyloxypropyl)phosphates) and mono(methacryloyloxyalkyl)phosphates (for example, mono(methacryloyloxyethyl)phosphate and mono(3-methacryloyloxypropyl)phosphate).

Especially preferred vinyl anionic monomers are acrylic acid, itaconic acid,  $\beta$ -carboxy ethyl acrylate, maleic acid and most especially methacrylic acid.

Preferred cationic monomers are those comprising substituted amine, quaternary amine, pyridine, guanidine and biguanidine groups. Especially preferred cationic acrylic monomers include dimethyl amino ethyl (meth)acrylate, diethyl amino ethyl (meth)acrylate, vinyl pyridine, dimethyl amino propyl methacrylamide and dimethyl amino butyl acrylate. These can be in the form of the free base (unprotonated), in the form of salt or in the form of a quaternary ammonium salt.

Preferred hydrophobic vinyl monomers have no hydrophilic groups. Preferred hydrophobic vinyl monomers include C<sub>1-20</sub>-hydrocarbyl (meth)acrylates, butadiene, styrene and vinyl naphthalene. Especially preferred C<sub>1-20</sub>-hydrocarbyl (meth)acrylates are butyl

(meth)acrylate, octyl (meth)acrylate, 2-ethyl hexyl (meth) acrylate, isobornyl acrylate, lauryl acrylate and stearyl acrylate.

Polyesters are typically made by esterification of a dicarboxylic acid with a diol. In place of the carboxylic acid an acid chloride, anhydride or alkyl (typically methyl or ethyl) ester of the acid can be used. Small amounts of monofunctional and/or tri or higher functional monomers can be used. Mixtures of carboxylic acids and/or alcohols can be used. Another route to the preparation of polyesters is the reaction of cyclic lactones such a method is typical for monomers such as caprolactone. Also caprolactone polymers can be reacted to give diols which may be used in both polyester or polyurethane synthesis.

Preferred hydrophobic monomers for making polyesters are esters, acids, acid chlorides anhydrides, cyclic lactones and alcohols containing C<sub>1-50</sub>-hydrocarbylene more preferably C<sub>4-50</sub>-hydrocarbylene, and especially C<sub>6-20</sub>-hydrocarbylene residues. These can be alkylene, cycloalkylene, arylene, aralkylene, alkarylene. These preferably contain no hydrophilic groups other than those needed for the polyester polymerisation. Other preferred hydrophobic monomers include those containing C<sub>3-4</sub>-alkyleneoxy (especially propyleneoxy which may comprise up to 50% ethyleneoxy by weight), fluorocarbons and siloxanes. Hydrophobic urethanes, polycarbonates and polyvinyls can be prepared with carboxylic acid or hydroxy groups such that they may be incorporated into polyesters.

Preferred hydrophilic monomers for making polyesters contain hydroxy groups and/or acid groups which are unreacted, or ethyleneoxy (which may comprise up to 50% by weight propyleneoxy).

Especially preferred are polyethyleneoxy polyols.

Suitable hydrophilic monomers for making polyesters may comprise sulphonic acid with hydroxy and/or carboxylic acid groups, for example aromatic dicarboxylic acids having an ionised sulphonate group. Particularly preferred is sodio-5-sulphoisophthalic acid (SSIPA). Other useful monomers which have two or more groups which readily undergo an ester condensation reaction and have one or more sulphonic acid groups are dihydroxy aryl monomers having at least one sulphonate group.

Since the polyester reaction is itself determined by the amounts and reactions of acids and hydroxy groups a further method of preparing hydrophilic polyesters is to use a non-stoichiometric excess of either the acid or the hydroxy group, or to use stoichiometric equivalence of these groups but not to complete the polyester synthesis to full conversion leaving some hydrophilic groups unreacted. An alternative method for introducing hydrophilic residues is to incorporate polyester monomers containing protected hydrophilic groups which are de-protected after polymerisation. The advantage of protection/de-protection is that the molecular weight and remaining acid/hydroxy functionality can be more separately controlled.

Polyurethanes are preferably made by the condensation of a di-isocyanate with a diol. Small amounts of monofunctional and/or tri or higher functional monomers can be used. Mixtures of isocyanates and/or alcohols can be used.

Preferred hydrophobic monomers for making polyurethanes include isocyanates and alcohols comprising C<sub>1-50</sub>-hydrocarbylene more preferably C<sub>4-50</sub>-hydrocarbylene, and especially C<sub>6-20</sub>-hydrocarbylene residues. These can be alkylene, cycloalkylene, arylene, aralkylene and alkarylene. Preferably the hydrophobic monomers contain no hydrophilic group other than those needed for the urethane polymerisation. Alternative preferred hydrophobic monomers for making polyurethanes contain siloxane and fluorocarbon groups. Hydrophobic polycarbonates, polyesters and polyvinyls can be prepared with isocyanate or hydroxy groups such that they can be incorporated into a polyurethane.

Examples of suitable hydrophobic isocyanates include ethylene diisocyanate, 1,6-hexamethylene diisocyanate, isophorone diisocyanate, tetramethylxylene diisocyanate, 1,4-phenylene diisocyanate, 2,4-toluene diisocyanate, 2,6-toluene diisocyanate, 4,4'-diphenyl-methane diisocyanate and its hydrogenated derivative, 2,4'-diphenylmethane diisocyanate and its hydrogenated derivative, and 1,5-naphthylene diisocyanate. Mixtures of the polyisocyanates can be used, particularly isomeric mixtures of the toluene diisocyanates or isomeric mixtures of the diphenylmethane diisocyanates (or their hydrogenated derivatives), and also organic polyisocyanates which have been modified by the introduction of urethane, allophanate, urea, biuret, carbodiimide, uretonimine or isocyanurate residues.

Preferred hydrophobic alcohols contain C<sub>3-4</sub>-alkyleneoxy (especially propyleneoxy which may comprise up to 50% ethyleneoxy by weight), fluorocarbon, siloxane, polycarbonate and C<sub>1-20</sub>-hydrocarbyl poly (meth)acrylate residues.

Preferred examples of hydrophobic diols for making polyurethanes include hexane diol, cyclohexane diol, propyleneoxy diols (which may comprise up to 50% ethyleneoxy by weight), diols from polycaprolactone, diols from polyvalerolactone, polyC<sub>1-20</sub>-alkyl (meth)acrylate diols, siloxane diols, fluoro carbon diols and alkoxylated bisphenol A.

Preferred hydrophilic monomers for making polyurethanes contain ethyleneoxy, ethyleneoxy-co-propyleneoxy, acidic groups or quaternary ammonium groups. Preferred examples of such monomers containing acidic groups are bis(2-hydroxyethyl)-5-sodiosulphoisophthalate and dihydroxy alcanoic acids, especially 2,2-dimethylol propionic acid. Preferred examples of such monomers containing quaternary ammonium groups are quaternary ammonium salt diols for example dimethanol diethyl ammonium bromide. The acidic and quaternary ammonium group may be in the form of a salt as hereinbefore described. A preferred polyurethane monomer containing an ethyleneoxy groups is polyetheneoxide diol and especially the polyoxalkylene amines as described in EP317258 the teaching of which is incorporated herein.

Alternatively hydrophilic residues can be introduced into polyurethanes by using excess hydroxy groups over isocyanate groups so that the resulting hydrophilic polyurethanes have unreacted hydroxy groups after polymerisation. In addition, monomers containing protected hydrophilic groups such as carboxylic acid and hydroxy groups can also be used which are later deprotected.

The dispersant is preferably chosen to suit the liquid medium to be used in the process for preparing the encapsulated particulate solid and optionally also the liquid vehicle to be used in the final intended composition in which the encapsulated particulate solid will be used (e.g. on inks). Thus for example where the encapsulated particulate solid is to be used in an aqueous ink jet ink the dispersant preferably has a predominantly hydrophilic character. Similarly where the encapsulated particulate solid is to be used in an oil-based paint or ink the dispersant preferably has a predominantly hydrophobic character.

The acid value (AV) of the dispersant is preferably from 10 to 200, more preferably from 30 to 150 and especially from 60 to 120mg KOH / g of the dispersant.

Preferably the dispersant has a number average molecular weight of from 500 to 100,000, more preferably from 1,000 to 50,000 and especially from 1,000 to 35,000.

The dispersant need not be totally soluble in the liquid medium. That is to say perfectly clear and non-scattering solutions are not essential. The dispersant may aggregate in surfactant-like micelles giving slightly hazy solutions in the liquid medium. Further the dispersant may be such that some proportion of the dispersant tends to form a colloid or particulate dispersion. It is preferred that the dispersant produces uniform and stable dispersions in the liquid medium which do not settle or separate on standing.

It is preferred that the dispersant is substantially soluble in the liquid medium giving rise to clear or hazy solutions.

Preferred random dispersants tend to give clear compositions whilst less preferred dispersants with two or more segments tend to give rise to the aforementioned hazy compositions in liquid media.

## 25 CROSS-LINKING AGENT

The cross-linking groups in the cross-linking agent must be reactive towards the cross-linkable group or groups in the dispersant. Two types of cross-linking reaction are preferred. The most preferred type of cross-linking reaction is nucleophilic attack by a cross-linking group to the carbon in the carbonyl group(s) from the ketoaldehyde or beta-diketoester cross-linkable group. Thus the preferred cross-linking groups for this type of reaction are nucleophiles, preferred examples being selected from amine, imine, hydrazide and thiol groups. These nucleophilic cross-linking agents may be low molecular weight (especially those having a number averaged molecular weight of less than 1000) or they may be polymeric (having a number averaged molecular weight of more than 1000). Preferred low molecular weight nucleophilic cross-linking agents include aliphatic diamines, hydroxy functional aliphatic diamines, and hydrazides. Preferred examples of which include diethylene triamine, triethylene tetramine, hexamine diamine hydrazine and adipic acid dihydrazide. Preferred polymeric nucleophilic cross-linking agents are polyamines, amine terminated polyoxyalkylene polymers (especially Jeffamines<sup>TM</sup>) and especially polyimines. Preferred polyamines include polyvinylamine, polyallylamine and

poly (4-amino styrene). Preferred polyimines include polypropyleneimine and especially polyethyleneimine.

The second type of cross-linking reaction involves the formation of an enolate anion or carbanion (depending on the tautomeric structure) in a carbon adjacent to a ketone, aldehyde or beta-diketoester carbonyl group. The formation of the enolate anion or carbanion is achieved by the addition of a base to the dispersant. Enolate anion or carbanion formation with beta-diketoesters can be achieved in with far milder bases (such as hydroxides, bicarbonates and amines) than those for aldehydes and ketones ( such as metal hydrides and organo alkali bases). Thus for this cross-linking type beta-diketoesters are much preferred. The enolate anion or carbanion from the dispersant can then be cross-linked with a cross-linking agent having electrophilic cross-linking groups. Thus the preferred cross-linking groups for this type of reaction are electrophiles, preferred examples being selected from activated olefinic, diazonium and carbonyl-containing groups. Especially preferred activated olefinic groups are acrylate groups.

The cross-linking groups present in a cross-linking agent may be the same or different. Two or more cross-linking agents can also be used. Where more than one cross-linking agent is used these may have a different number of cross-linking groups and/or may use different types of cross-linking groups.

The cross-linking agent is preferably soluble in the liquid medium.

## PROCESS PREFERENCES

Preferably the cross-linking is performed by mixing the particulate solid, the dispersant, the cross-linking agent and the liquid medium. Preferably the weight ratio of the particulate solid to liquid medium is from 1:100 to 1:2.5, more preferably 1:100 to 1:3, especially 1:100 to 1:5. Preferably the weight ratio of the dispersant to the liquid medium is 1:1000 to 1:2.5, more preferably 1:100 to 1:3.3, especially 1:100 to 1:5. Preferably the cross-linking agent is present in the liquid medium at a concentration such that the molar ratio of cross-linking groups in the crosslinking agent to the cross-linkable groups in the dispersant is from 10:1 to 1:10, more preferably from 1:5 to 5:1 and especially from 1:2 to 1:2. This typically equates a weight ratio of cross-linking agent to liquid medium of 1:1000 to 1:10, more preferably 1:100 to 1:20.

Thus preferably the cross-linking is performed by mixing the following ingredients:

- a) a liquid medium;
- b) a particulate solid in a weight ratio of 1:100 to 1:3, more preferably 1:100 to 1:5;
- c) the dispersant in a weight ratio of 1:100 to 1:3.3, more preferably 1:100 to 1:5; and
- d) the cross-linking agent in a weight ratio of 1:10000 to 1:10; more preferably 1:2000 to 1:20;

wherein all weight ratios are relative to the weight of the liquid medium.

Preferably the mixing is performed at a temperature below 60°C. This may be performed by any method, e.g. mechanical agitation, stirring and so on. Low temperatures for cross-linking are preferred as this results in lower levels of flocculation and particle size growth of the particulate solid in the liquid medium. Preferably the cross-linking is 5 performed at a temperature of less than 60°C, more preferably less than 40°C and especially at less than 30°C. The lower temperature limit for cross-linking is determined by the freezing point of the liquid medium and the desired rate of reaction but a preferred lower limit is 0°C.

10 The time for the cross-linking depends to some extent on the temperature and presence or absence of a catalyst. However a preferred time is from 1 to 24 hours, more preferable from 1 to 8 hours. If desired a catalyst may be added to speed up the reaction.

15 The particulate solid, the liquid medium and the dispersant may be mixed in any order, or simultaneously. The mixture may be subjected to a mechanical treatment to reduce the particle size of the solid to a desired size, for example by ball milling, bead milling, gravel milling or by more elaborate techniques such as microfluidizing (using a Microfluidics™ machine) or using hydrodynamic cavitation (using for example the CaviPro™ device) until a dispersion is formed. Alternatively, the particulate solid may be treated to reduce its particle size independently or in admixture with either the liquid 20 medium or the dispersant, the other ingredient or ingredients then being added and the mixture being agitated to provide the dispersion.

25 If desired the dispersion may be filtered or centrifuged to remove any poorly dispersed or oversized particulate material prior to cross-linking. In particular the process preferably comprises filtering a mixture comprising the dispersant, a particulate solid and liquid medium prior to cross-linking, preferably through a filter having a pore size of less than 10, more preferably less than 5 and especially less than 1 micron.

30 If the cross-linking agent is present during mechanical treatment of the particulate solid this can result in undesirable pre-cross-linking of the dispersion before the particle size of the solid has been fully reduced. When the particulate solid is milled in the presence of the dispersant and the liquid medium the temperature is preferably not greater than 40°C and especially not greater than 30°C.

35 The cross-linking agent is preferably added to a mixture comprising the particulate solid, dispersant and liquid medium after mechanical treatment to reduce the particle size of the particulate solid. Cross-linking can occur whilst the cross-linking agent is being added but it is more preferred that the greater part of the cross-linking occurs after complete addition of the cross-linking agent. It is also preferred that less than 10% cross-linking has occurred 30mins after the complete addition of the cross-linking agent. This facilitates more uniform dispersion of the cross-linking agent throughout the composition and results in more uniform cross-linking.

40 To inhibit cross-linking whilst the cross-linking agent is being added to a mixture comprising the particulate solid, dispersant and liquid medium the cross-linking agent is

preferably added to said mixture at a temperature below 60°C and especially below 30°C. Also it is preferred that where the process uses a catalyst to increase the speed of crosslinking this is added after the addition of the cross-linker.

5 The process preferably results in an encapsulated particulate solid having a volume average particle size of at most 50% greater than the volume average particle size of the particulate solid prior to addition of the cross-linking agent.

Preferably the encapsulated particulate solids have a volume average particle size of less than 300nm, more preferably from 10 to 300nm, because such particles are particularly useful in paints, inks and especially in ink jet printing inks.

10 The volume average particle size may be measured by any means known but a preferred method is via photo correlation spectroscopy techniques as available from Malvern™ and Coulter™.

#### ENCAPSULATED SOLID

15 If desired the process may further comprise the step of isolating the resultant encapsulated particulate solid from the liquid medium. This may be achieved by, for example, evaporating the liquid medium, or by precipitation or flocculation of the encapsulated particulate solid followed by filtration.

20 Preferred methods of evaporation include freeze drying, spray drying and agitated drying. Preferred methods of precipitation and flocculation include the addition of metal salts, freeze/thawing and centrifugation.

25 The process of the present invention is capable of being performed at lower temperatures than are suitable for cross-linking dispersants having alternative cross-linking groups. This results in reduced levels of flocculation and minimal growth in particle size. In ink jet printing large particles are undesirable because they can block the tiny nozzles used in print heads. Furthermore, the ability to use low temperatures enables encapsulation and dispersion of temperature-sensitive particulate solids, e.g. pharmaceuticals and agrochemicals.

30 According to a second aspect of the present invention there is provided an encapsulated particulate solid obtainable or obtained by the process of the first aspect of the present invention.

#### COMPOSITIONS AND INKS

35 The encapsulated particulate solid prepared by the process of the present invention is useful in the manufacture of compositions comprising the encapsulated particulate solid and a liquid vehicle. Preferably such compositions are inks and the particulate solid is a colorant, especially a pigment.

40 Thus according to a third aspect of the present invention there is provided a composition comprising a liquid vehicle and an encapsulated particulate solid obtained or obtainable by a process according to the first aspect of the present invention.

The compositions may be prepared by diluting the product of the process, or by isolating the product of the process and mixing the isolated encapsulated particulate solid with a liquid vehicle. It is preferable to prepare the composition by adding desired liquid vehicle components to the composition comprising the encapsulated particulate solid and the liquid medium resulting from the process according to the first aspect of the present invention. This process, which does not isolate the encapsulated particulate solid, tends to result in smaller particle size of the encapsulated particulate solid.

#### THE LIQUID VEHICLE

The liquid vehicle may be identical to or different from the liquid medium used in the process for preparing the encapsulate solid. It is often desirable that the liquid vehicle comprises high proportions of water and that further liquids required to make the desired composition or (e.g. an ink) are added after the process according to the first aspect of the present invention.

The liquid medium is preferably an organic solvent or water or a mixture thereof.

Preferably the liquid vehicle comprises water, especially when the compositions are intended for use in ink jet printing. Preferably the liquid vehicle comprises from 50 to 95% more preferably from 60 to 95% and especially from 60 to 90% water by weight based on the total weight of the composition.

In the case of ink jet printing compositions it is preferable that the liquid vehicle comprises both water and an organic solvent which is preferably a water-miscible organic solvent. Preferred water-miscible organic solvents for inclusion into the liquid vehicle include C<sub>1-6</sub>-alkanols, preferably methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol, n-pentanol, cyclopentanol and cyclohexanol; linear amides, preferably dimethylformamide or dimethylacetamide; water-miscible ethers, preferably tetrahydrofuran and dioxane; diols, preferably diols having from 2 to 12 carbon atoms, for example ethylene glycol, propylene glycol, butylene glycol, pentylene glycol, hexylene glycol and thiodiglycol and oligo- and poly-alkyleneglycols, preferably diethylene glycol, triethylene glycol, polyethylene glycol and polypropylene glycol; triols, preferably glycerol and 1,2,6-hexanetriol; mono-C<sub>1-4</sub>-alkyl ethers of diols, preferably mono-C<sub>1-4</sub>-alkyl ethers of diols having 2 to 12 carbon atoms, especially 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy)-ethanol, 2-[2-(2-methoxyethoxy) ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)-ethoxy]-ethanol and ethyleneglycol monoallylether; cyclic amides, preferably 2-pyrrolidone, N-methyl-2-pyrrolidone, N-ethyl-2-pyrrolidone, caprolactam and 1,3-dimethylimidazolidone. Preferably the liquid vehicle comprises water and 2 or more, especially from 2 to 8, water-miscible organic solvents.

Especially preferred water-miscible organic solvents are cyclic amides, especially 2-pyrrolidone, N-methyl-pyrrolidone and N-ethyl-pyrrolidone; diols, especially 1,5-pentane diol, ethyleneglycol, thiodiglycol, diethyleneglycol and triethyleneglycol; and mono- C<sub>1-4</sub>-alkyl and C<sub>1-4</sub>-alkyl ethers of diols, more preferably mono- C<sub>1-4</sub>-alkyl ethers of diols having 2 to 12

carbon atoms, especially 2-methoxy-2-ethoxy-2-ethoxyethanol; and glycerol.

A preferred composition comprises:

- a) from 0.1 to 50 parts, more preferably from 1 to 25 parts, of an encapsulated particulate solid obtainable or obtained by a process according to the first aspect of the present invention;
- b) from 50 to 99.9 parts, more preferably from 99 to 75 parts, of a liquid vehicle comprising water, an organic solvent or both water or an organic solvent; wherein all parts are by weight, components a) and b) add to 100 parts.

The weight ratio of water to organic solvent when both are present in the liquid vehicle is preferably in the range 99:1 to 5:95, more preferably 95:5 to 60:40, especially 95:5 to 80:20.

The compositions of the present invention are particularly suitable for ink jet printer inks, especially where the particulate solid is a pigment.

In the case of ink jet printing the composition according to the third aspect of the present invention preferably has a viscosity of less than 50mPa.s, more preferably less than 20mPa.s and especially less than 10mPa.s at a temperature of 25°C.

In the case of ink jet printing it is preferred that the composition according to the third aspect of the present invention preferably has a surface tension from 20 to 65 dynes/cm, more preferably from 25 to 50 dynes /cm.

The ink jet printing compositions of the present invention may also contain additional components conventionally used in ink jet printing inks, for example viscosity modifiers, pH buffers (e.g. 1:9 citric acid/sodium citrate) corrosion inhibitors, biocides, binders, dyes and kogation reducing additives.

According to a fourth aspect of the present invention there is provided a process for printing an image on a substrate comprising applying a composition according to the third aspect of the present invention to the substrate, preferably by means of an ink jet printer.

According to a fifth aspect of the present invention there is provided a paper, a plastic film or a textile material printed with a composition according to the third aspect of the present invention, preferably by means of an ink jet printer. Preferred papers are plain or treated papers which may have an acid, alkaline or neutral character. Examples of commercially available papers include, HP Premium Coated Paper, HP Photopaper (all available from Hewlett Packard Inc), Stylus Pro 720 dpi Coated Paper, Epson Photo Quality Glossy Film, Epson Photo Quality Glossy Paper (available from Seiko Epson Corp.), Canon HR 101 High Resolution Paper, Canon GP 201 Glossy Paper, Canon HG 101 High Gloss Film (all available from Canon Inc.), Wiggins Conqueror paper (available from Wiggins Teape Ltd), Xerox Acid Paper and Xerox Alkaline paper, Xerox Acid Paper (available from Xerox).

The plastic film may be opaque or transparent. Transparent plastic films which are suitable for use as overhead projector slides, include for example polyesters (especially

polyethylene terephthalate), polycarbonates, polyimides, polystyrenes, polyether sulphones, cellulose diacetate and cellulose triacetate films.

According to a sixth aspect of the present invention there is provided an ink jet printer cartridge comprising a chamber and a composition according to the third aspect of the 5 present invention wherein said composition is present in the chamber.

## COATINGS AND PAINTS

Encapsulated particulate solids obtainable or obtained by the process of the present invention are particularly suitable for use in surface coatings and paints which 10 comprise an encapsulated particulate solid, a liquid vehicle and a binder. The particulate solid is preferably a colorant or a filler. As with inks the paint can be made using the isolated encapsulated particulate solid but it is more preferred to use the composition comprising the encapsulated particulate solid and the liquid medium which results from the process according to the first aspect of the invention. Thus according to an seventh. 15 aspect of the present invention there is provided a composition comprising an encapsulated particulate colorant or filler obtainable or obtained by a process according to the first aspect of the present invention, a binder and a liquid vehicle. The binder is a polymeric material capable of binding the composition on the volatilisation of the liquid medium.

20 Suitable binders include natural and synthetic polymers. Preferred binders include poly(meth)acrylates, polystyrenics, polyesters, polyurethanes, alkyds, polysaccharides (e.g. cellulose) and proteins (e.g. casein). Preferably the binder is present in the composition at more than 100%, more preferably 200%, especially 300% and most preferably more than 400% based on the weight of the particulate solid.

25 The invention is further illustrated by the following Examples in which all parts and percentages are by weight unless otherwise stated.

### Example 1

#### 30 Preparation of Dispersant (1)

A monomer feed composition was prepared by mixing methacrylic acid (25.82 parts), acetoacetoxyethylmethacrylate (128.54 parts), 2-ethylhexylmethacrylate (45.64 parts) and isopropanol (100 parts). An initiator feed composition was prepared by mixing 2,2'-azobis(2-methylbutyronitrile) (7.25 parts) and isopropanol (50 parts).

35 Isopropanol (50 parts) was heated to reflux in a reactor vessel, continuously stirred and purged with a nitrogen gas atmosphere. The monomer feed and the initiator feed compositions were slowly fed into the reactor vessel whilst stirring the contents, heating to reflux and maintaining a nitrogen atmosphere. The monomer feed was fed into the reactor over 2 hours and the initiator feed was fed in over 3 hours. Reflux heating of the 40 reactor vessel contents was continued for a further hour after complete addition of the

initiator feed before cooling to 25°C. The product obtained was an acrylic polymer solution with a solids content of 49.6% by weight. The solvent and unreacted monomers were removed from the acrylic polymer solution by evaporation at reduced pressure to give a solid acrylic polymer of number average molecular weight 14,188, weight average molecular weight 39,386 and polydispersity 2.7 as measured by GPC. This is Dispersant (1).

#### Dispersant Solution 1

Dispersant (1) (15 parts) was dissolved in water (85 parts) and neutralised with potassium hydroxide aqueous solution to give an aqueous solution of pH 8.1. This is Dispersant Solution (1).

#### Mill-base (1)

A particulate solid (C.I. Pigment Blue 15:3, 120 parts, ex Clariant) was mixed with Dispersant Solution (1) (80 parts) and deionised water (588 parts). The mixture was milled in an Eiger mill for a period of 3 hours. This resulted in a mill-base comprising a particular solid of average particle size of 136nm and a pigment content of 15%ww. This is Mill-base (1).

#### Cross-linking of Dispersent (1) to Encapsulate a Particulate Solid

A cross-linking agent (Diethylene triamine, 0.077 parts) was slowly added to Mill-base (1) (50 parts) and the mixture was stirred for 6 hours at a temperature of 40 to 50°C. The resulting encapsulated particulate solid had an average particle size of 161nm which had increased in size by only 18%. This is Encapsulated Particulate Solid (1).

25

#### Tests

##### Thermal Stability

Samples of Mill Base (1) and Encapsulated Particulate Solid (1) were stored at a temperature of 60°C for duration of 2 weeks. After this time the particle size was remeasured and the percentage growth was calculated. Table 1 summaries the results.

Table 1

<u>Sample</u>	<u>%Growth</u>
Mill-base (1)	22.4
Encapsulated Particulate Solid (1)	9.9

5       Table 1 shows that the compositions of the present invention show superior thermal stability to uncross-linked equivalents.

#### Solvent Resistance

10      The resistance of Mill-base (1) and Encapsulated Particle Solid (1) to organic liquids was measured by adding them to butoxy ethanol/water mixtures. Mill-base (1) was intolerant to the presence of butoxy ethanol and showed severe coagulation in compositions containing 90 parts water and 10 parts butoxy ethanol. Encapsulated Particulate Solid (1) was stable even in neat (100%) butoxy ethanol. Thus the composition of the present invention shows much improved solvent resistance.

CLAIMS

1. A process for preparing an encapsulated particulate solid comprising cross-linking a dispersant with a cross-linking agent in the presence of a particulate solid and a liquid medium, thereby encapsulating the particulate solid within the cross-linked dispersant, characterised in that :

- a) the dispersant has at least one cross-linkable group selected from keto, aldehyde and beta-diketoester groups; and
- b) the cross-linking agent has at least two cross-linking groups reactive towards said cross-linkable group(s).

10 2. A process according to claim 1 wherein the cross-linking agent is soluble in the liquid medium.

15 3. A process according to any one of the preceding claims wherein the cross-linking groups are nucleophiles.

4. A process according to claim 3 wherein the cross-linking groups are selected from amine, imine, hydrazide and thiol groups.

20 5. A process according to claims 1 or 2 wherein the cross-linking groups are electrophiles.

25 6. A process according to claim 5 wherein the cross-linking groups are selected from activated olefinic, diazonium and carbonyl-containing groups.

7. A process according to any one of the preceding claims wherein the dispersant is polymeric.

30 8. A process according to claim 7 wherein the dispersant is a polyvinyl dispersant.

9. A process according to claim 8 wherein the polyvinyl dispersant comprises at least one monomer residue selected from the group consisting of acrolein, methyl vinyl ketone, diacetone acrylamide and acetoacetoxyl ethylmethacrylate.

35 10. A process according to any one of the preceding claims wherein cross-linking is performed at a temperature of less than 60°C.

40 11. A process according to any one of the preceding claims wherein the resulting encapsulated particulate solid has a volume average particle size of at most 50% greater

than the volume average particle size of the particulate solid prior to addition of the cross-linking agent.

5 12. A process according to any one of the preceding claims wherein the liquid medium comprises water.

13. A process according to any one of the preceding claims comprising the further step of isolating the resultant encapsulated particulate solid from the liquid medium.

10 14. A process according to any one of the preceding claims wherein cross-linking is performed by mixing the following ingredients:

- a) a liquid medium;
- b) a particulate solid in a weight ratio of 1:100 to 1:3;
- c) the dispersant in a weight ratio of 1:100 to 1:3.3; and
- 15 d) the cross-linking agent in a weight ratio of 1:10000 to 1:10;

wherein all weight ratios are relative to the weight of the liquid medium.

15 16. An encapsulated particulate solid obtainable by a process according to any one of the preceding claims.

20 17. A composition comprising a liquid vehicle and an encapsulated particulate solid according to claim 15.

25 18. A composition according to claim 16 having a viscosity of less than 20mPa.s at 25°C.

19. A composition according to claim 16 or 17 wherein the liquid vehicle comprises water and an organic solvent in a weight ratio of 99:1 to 5:95.

30 20. A process for printing an image on a substrate comprising applying a composition according to claim 17 or 18 to the substrate.

21. A process according to claim 19 wherein the printing is performed by means of an ink jet printer.

35 22. A paper, a plastic film or a textile material printed with a composition according to claim 16, 17 or 18 by means of a process according to claim 19 or 20.

22. An ink jet printer cartridge comprising a chamber and a composition wherein the composition is present in the chamber and the composition is as claimed in claim 16, 17 or 18.

5 23. A composition according to claim 16 where the particulate solid is a colorant or filler and the composition further comprises a binder.

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